Aqueous Absorption of NO_x Induced by Sodium Chlorite Oxidation

BY

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ABSTRACT

Title of thesis : Aqueous Absorption of NO_x Induced by Sodium Chlorite Oxidation

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Aqueous scrubbing in alkaline media for the removal of nitrogen oxides (NO_x) from flue gases using $NaClO_2$ as an oxidant is being investigated in the Chemical Engineering Department of New Jersey Institute of Technology. This thesis presents the findings of an experimental program that was conducted to estimate the capability of $NaClO_2$ aqueous solution to oxidize insoluble NO to soluble NO_2 in order to increase its solubility and thus prevent NO_x emission from entering the atmosphere from flue gases emitted by municipal incinerators or power plants.

The key findings of this program are:

* NO is not absorbed by NaOH aqueous scrubbing solutions.
* NO_2 is essentially quantitatively absorbed in NaOH aqueous scrubbing solutions.
* Addition of NO_2 improves NO absorption in NaOH solution.
* $NaClO_2$ containing aqueous scrubbing medium quantitatively oxidizes NO to nitrate.

* Concentrations greater than 0.1M NaOH inhibit NO absorption in 0.008M $NaClO_2$ containing aqueous scrubbing media.

* Aqueous scrubbing media containing less than 0.1M NaOH quantitatively absorb NO induced by $NaClO_2$ oxidation.

* The presence of 5% Oxygen in flue gases reduces by 11.5% NO absorption induced by $NaClO_2$ oxidation.

* Mass transfer rather than chemical reaction kinetics seems to dominate the NO absorption process.

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ABSTRACT

1. INTRODUCTION

Nitrogen oxides (NO_x) are mixtures of compounds of nitrogen and oxygen, namely, N_2O, NO, N_2O_3, NO_2, N_2O_4 and N_2O_5 generally found in effluents from combustionsources. The predominant NO_x compounds are NO and NO_2. They are formed as a result of the reactions of atmospheric nitrogen with atmospheric oxygen at high temperatures. Also, large quantitative of NO_x are formed from the oxidation of nitrogen compound found in fuel or in wastes being incinerated. More than 90% of NO_x emitted from stationary combustion sources consist of NO which is relatively insoluble in inorganic aqueous solution. finding a way to control NO is essential for the prevention of NO_x pollution.

The molecular and thermodynamic properties of NO according to Yost and Russel (1944) are sumarized in Table 1 . Its bonding type can be studied by magnetic measurements, by which the participation of the odd electron in the bond is probed, or by measuring the change in the bond strength between nitrogen and oxygen atoms, as manifested by its infrared spectra. The configuration of NO molecular orbitals and the bonding of the nitric oxide group is illustrated in Figure 1 (M. Shelef 1971).

1-1 NO_x formation and sources

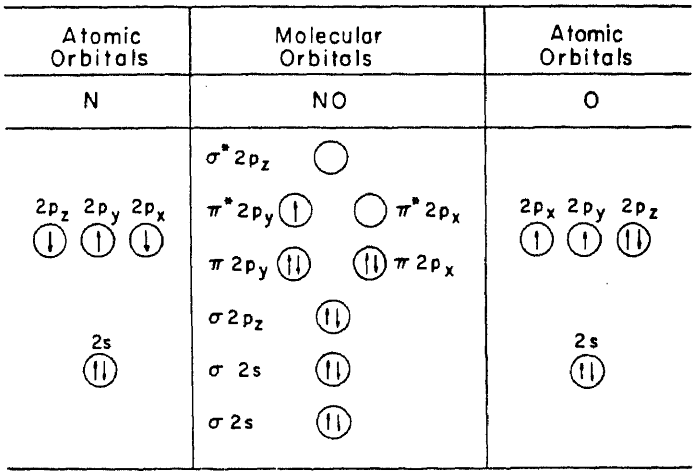
Nitrogen oxides are emitted as nitric oxide (NO) from a variety of sources. The estimated emissions of NO_x have large uncertainties associated with them. About 70-90% of Atmospheric

NO_X emission are from anthropogenic sources in the world (Singh 1987).

Table 1 Molecular and Thermodynamic properties of NO

Molecular Properties		Thermodynamic Properties	
Bond energy	151 Kcal/Mole	m.p.	109.49°K
Bond length	1.15 Å	ΔH fusion	549.5 cal/mole
1st ionization potential	9.5 V	b.p.	121.36°K
Dipole moment	0.16 Debye	ΔH vaporization	3293 cal/mole
Molal susceptibility, 20°C	$1.43 \cdot 10^{-3}$ cgs units	$\Delta H^{o}{}_{f,298K}$	+21,500 cal/mole
Ground state	$^{2}\Pi_{1/2}$	$\Delta F^{o}{}_{f,298K}$	+20,650 cal/mole
1st excited state	$^{2}\Pi_{3/2}$	$\Delta S^{o}{}_{f,298K}$	50.35 e.u.
$\Delta E(^{2}\Pi_{1/2} \rightarrow {}^{2}\Pi_{3/2})$	352 cal/mole (124.2 cm^{-1})		

Figure 1 Bonding and Electron configuration of NO



1-1-1 Fossil fuel combustion and biomass burning

Thermally generated NO_x results from the reactions of oxygen-nitrogen mixture exposed to a high temperature. The maximum concentration of NO_x can be estimated from the equilibrium composition of an oxygen-nitrogen mixtures as a function of temperature (Shelef, 1971). The equilibrium compositions of NO as a function of temperature are summarized in Table 2.

The key chemical reactions in the oxygen-nitrogen mixture at temperature below 4,500 K are given in Table 3. Dissociation of N_2 into atomic nitrogen becomes important above 4,500K. (Seinfeld, 1986).

1-1-2 Lightning

The major natural source of NO_x is caused by the effect of atmospheric lightning on atmosphere oxygen and nitrogen. The temperature of a column of air exposed to atmospheric lightning is a function of energy deposition of the lightning. For a typical energy deposition of about 10^5 J/m, the column of air immediately surrounding the charge is heated to temperature on the order of 30,000K. At temperature above 2,300K, NO is in thermodynamic equilibrium with N_2 and O_2. As the temperature of the heated air drops below 2,000K, NO "freezes " as a stable compound.

The total global production of NO due to atmospheric

Table 2 Equilibrium Concentration of NO in Nitrogen-Oxygen Mixture

Temperature °K	K	Equilibrium NO Concentration, ppm
298	1.549×10^{15}	5.6×10^{-11}
400	1.413×10^{11}	6.15×10^{-7}
500	6.223×10^{8}	1.39×10^{-4}
600	1.663×10^{7}	5.2×10^{-3}
700	1.268×10^{6}	6.85×10^{-2}
800	1.828×10^{5}	4.75×10^{-1}
900	4.046×10^{4}	2.14
1,000	1.208×10^{4}	7.23
1,100	4.508×10^{3}	19.3
1,200	1.977×10^{3}	43.5
1,300	9.863×10^{2}	88.0
1,400	5.433×10^{2}	160.0
1,500	3.236×10^{2}	269.0
1,600	2.056×10^{2}	424.0
1,700	1.380×10^{2}	630.0
1,800	9.683×10^{1}	905.0
1,900	7.047×10^{1}	1230.2
2,000	5.297×10^{1}	1640.0

Table 3 Key Reactions of Nitrogen-Oxygen Mixture at High Temperature

Reaction	Forward Reaction cm^3 molecule^{-1} sec^{-1} [d]	Reverse Reaction cm^3 molecule^{-1} sec^{-1}
$O_2 + M \rightleftarrows 2O + M$ [c]	$1.876 \times 10^{-6} T^{-1/2} \exp(-118,000/RT)$	2.6×10^{-33} [b]
$O + N_2 \rightleftarrows NO + N$	$1.16 \times 10^{-10} \exp(-75,500/RT)$	2.57×10^{-11}
$N + O_2 \rightleftarrows NO + O$	$2.21 \times 10^{-14} T \exp(-7080/RT)$	$5.3 \times 10^{-15} T \times \exp(-39,100/RT)$

lightning is the product of two terms: 1) The yield of NO per energy input or lightning (J) or the NO per lightning flash and 2) the total energy deposited by lightning or the lightning flash frequency (Levine, 1984).

1-1-3 Microbial activity in soils

It has been found from field flux measurements and laboratory experiments that soil microrganisms may also produce appreciable amounts of NO. To quantify the rate of production of NO, a series of laboratory experiments were performed using two of the most common bacteria found in soils, Nitrosomonas Europaea and Alcaligenes Faecalis. The results indicate that nitrification is an aerobic process in which ammonium is oxidized to nitrite and nitrate. NO and N_2O are direct or indirect intermediates of this pathway (Levine, 1984).

1-1-4 Diffusion

NO_x diffusion from the stratosphere is also an important source of tropospheric NO_x.

1-2 Health effects of NO_x

Little data exists on the health effects of NO_x because exposure to these compounds is usually accompanied by concurrent exposure to other pollutants. Previous studies have demonstrated that NO_2 causes emphysema in several animal species.

EPA's "Cincinnati dog study" which used 0.64 ppm NO_2 in combination with 0.25 ppm NO, also indicated that the effect was progressive. The airway resistance of the lungs is known to increase when moderate exposures to NO_x occurs. The principal epidemiological study of the effects NO_2 was conducted on the population of Chattanooga, Tenessee, in 1978, where manufacturing operations produced an atmosphere contaminated primarily by this compound. A conclusion from this study is that respiratory illness aer higher than normal, if the concentration of NO_2 exceeds 0.06 ppm This study has been criticized for several reasons, but it remains the main source of data on the health effects of NO_2.

1-3 Legislation

Man-made NO_x emissions frequently accompany combustion. Various emission standards, limits and regulations have been promulgated to control NO_x emission. In the USA, the primary standard for nitrogen dioxide is $100ug/m^3$, taken as an annual arithmetic mean. But there is no standard for nitric oxide. Table 4 compare the emission standards of Sitzerland, Austria, Netherland, the FRG and Japan with the USA. The New Source Performance Standards for large utilities requires NO_x emissions not to exceed 86g/EJ for gaseous fuels, 130g/EJ for liquid fuels and 260g/EJ for solid fuels (taken as NO_2).

Tble 4. Emission Standards for New Power Plants

State	power (MW)	Fuel ($g\ MJ^{-1}$) solid	liquid	gas
Switzerland	> 300	0.07	0.04	0.03
	50-300	0.14	0.07	0.05
	1-50	0.18	0.07	0.05
Austria -Draft	> 300	0.05	0.03	0.02
	150-300	0.11	0.06	0.04
	50-150	0.11	0.08	0.05
Netherlands	> 300	0.14	0.08	0.05
	50-300	0.18	0.08	0.05
FRG	> 300	0.07	0.04	0.03
	50-300	0.14	0.08	0.05
	1-50	0.18	0.13	0.05
Japan	> 550	0.14	0.07	0.03
	400-550	0.18	0.07	0.03
	30-400	0.18	0.09	0.06
	5-30	0.25	0.09	0.07
	< 5	0.25	0.10	0.08
USA	> 73	0.28	0.14	0.09
	29-73	0.32	0.14	0.05

1-4 Technologies for NO_x control

Emission of NO_x has become a serious environmental problem and it is necessary for existing power plants plus municipal and industrial incinerators, utilizing high temperature processes, to remove the NO_x from flue gases in order to comply with federal and local regulations.

In the past few years, a variety of processes have been proposed to eliminate this problem. These processes can be summarized as follows:

A). Combustion modification

- Low NO_x burner design: Various burner designs have been proposed to lower the NO_x emission such as tangentially fired boiler. Traditional cyclone burners produced high concentration of NO_x in flue gas. Because the temperature of heat sinks of tangential firing burner almost equals to the temperature of burner flame, it reduces 50% to 60% thermal NO_x formation (Maulbetsch, 1986).
- Flue gas recirculation: Flue gas recirculation is an effective method to reduce thermal NO_x. The recirculated flue gas lowers the flame temperature and the oxygen contain in combustion. According to the report of EXXON research, 50% of flue gas recirculation reduces 60% thermal NO_x formation (Sommerlad, 1971), (Shaw, 1981).
- Air-fuel staging in the combustion chamber: Thermal NO_x formation can be reduced by operating the combustion in a fuel rich mode, followed by interstage cooling and burnout of the uncombusted compounds with excess air. Incomplete combustion in the first stage lowers thermal NO_x formation. The second stage uses excess air to complete the combustion, reduce the combustion temperature and lower the thermal NO_x formation (Bienstock, 1972). Alternatively, another method of interstage cooling can be used in order to

avoid a large excess of stoichiometic air.

B). Flue gas cleaning

- * Selective noncatalytic reduction: NO_x can be reduced to N_2 and H_2O by introduce NH_3 into the effluent gas from a combustor at 930 to 990°C. The major disadvantages of this process are the narrow temperature window, the need for well mixed NH_3 and the possibility that NH_3 may break through (Seinfeld, 1988).
- * Selective catalytic reduction: This process operates similiary to the thermal process except with a catalyst. The reactions occur at a much lower temperature of 300 to 400°C. There are commercial catalyst containing noble metals or vanadia/titania that can control NO_x by 90% for the former, and 80% by the latter. Much research is currently being conducted for using Zeolites to control NO_x with NH_3 (personal communication with Dr. Henry Shaw).
- * Adsorption by solids: A number of activated carbon processes have been proposed to remove NO from flue gas. Copper oxide is also an effective adsorbent. Using these processes, Technologies of adsorbent regeneration and SO_2 removal are essential (Seinfeld, 1988).
- * Wet process: In these processes, solvents are used to scrub NO from flue gases. chemical reaction is required

to absorb NO in water. Those chemical reactions can be categorized to Gas Phase oxidation, liquid phase oxidation and, chelating reduction.

The gas scrubbing research presented here was conducted in the Gas Scrubbing Laboratory (room 206 Advanced Technology Center) of NJIT since May 1988. It is categorized as liquid phase oxidation, In this process, NO_x is absorbed into alkaline solution and oxidized to nitrate.

2. GAS ABSORPTION

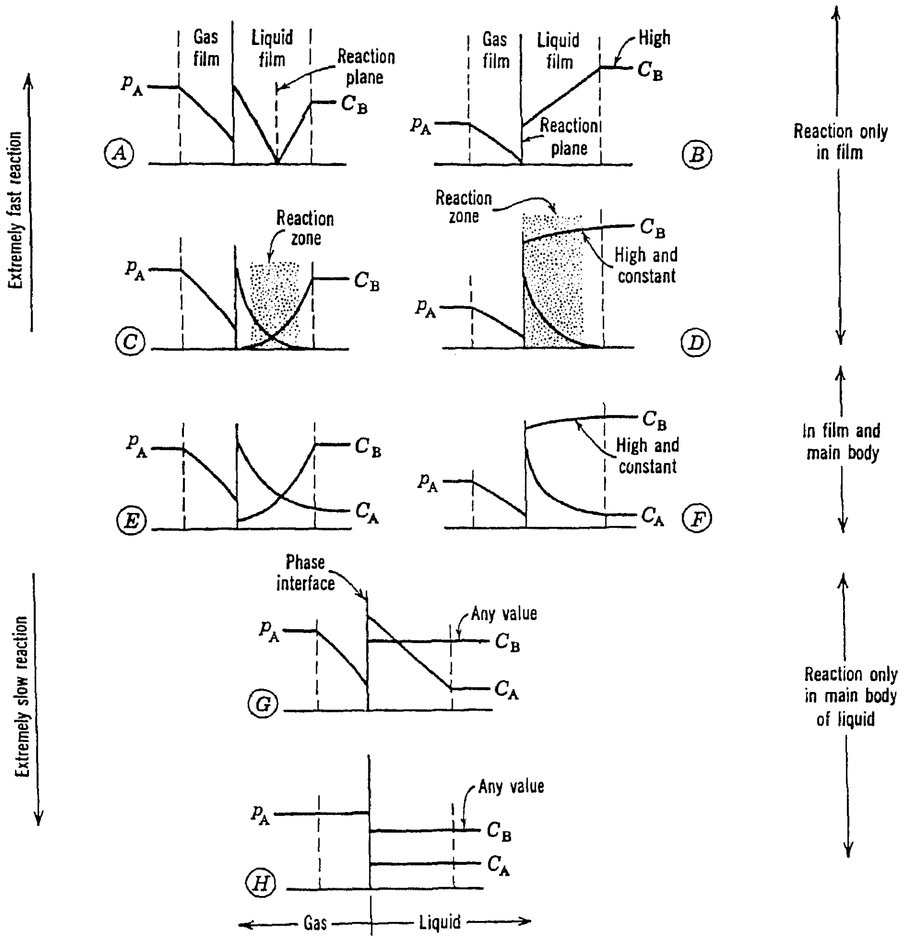
2-1 General concepts

Absorption is a diffusional process that involves the transfer molecules from the gas phase into the liquid phase because of the concentration gradient between the two phases. The removal of contaminant by gas absorption occurs by bringing the gas into contact with a liquid in which the contaminant alone are soluble. Absorption of any species occurs at the surface of the liquid film (e.g., surrounding the packing (or mesh) or at the bubble surface when the gas is the dispersed phase).

Absorption is a unit operation that is enhanced by all the factors which normally affect mass transfer. There are high interfacial area, turbulent contact between the two phases, increased residence time, repetive contact, high solubility, high diffusion coefficient, low liquid viscosity, and large negative Gibb's free energy changes in the case of reactive scrubbing. These factors influence the rate of mass transfer because they directly influence the concentration gradient.

The two film theory of gas absorption is the basic model of describing mass transfer from a gas to a liquid. The model is based on the theory that thin films exist on both sides of the phase boundary between gas and liquid. Molecular mass transfer or diffusion can only occur through these films. Figure 2 shows the interface behavior of two film theory for the complete range of the reaction rate and mass transfer rate.

Figure 2. Interface Behavoir of Two Film Theory



Case A,B,C and D: Reactions are so fast that component A is consumed before it diffuse into the main body of liquid. Reaction occurs only in the liquid film.

Case E and F: Reaction rates are intermediate with respect to mass transfer. Reaction will occur in both film and main body of the liquid.

Case G: Reaction rate is slow with respect to mass transfer. Reaction occurs in bulk liquid, however the film still provides a resistance of component A to transfer to the bulk liquid.

Case H: Reaction rate is infinitively slow with respect to mass transfer. Equilibrium is established and absorption is controled by chemical reaction only.

2-2 Physical absorption

The amount of a gas being physically absorbed in a liquid is determined by the solubility of the gas in the liquid. Solubility can be expressed in terms of partial pressure through Henry's Law as

$$P_a = H_a * X_a$$

Where H_a: Henry's Law constant of A

P_a: partial pressure of A

X_a: mole fraction of A in liquid phase

The mass transfer rate is the product between the mass transfer coefficient and the concentration difference between the bulk and the phase boundary.

$$N_a = K_a*(P_{ag}-P_{al})$$

In this case we may lump Henry's Law constant into the relation between overall mass transfer coefficient, K_a, gas phase mass transfer coefficient, K_{ag} and liquid phase mass transfer coefficient, K_{al}

$$\frac{1}{K_a} = \frac{1}{K_{ag}} + \frac{H_a}{K_{al}}$$

Henry's Law is obeyed, when

1) The concentration of disolved gas is very low.
2) The temperature and pressure are far away from the critical temperature and pressure of the gas, and
3) The gas does not change it's molecular structure when it disolves (Bethea, 1978).

Physical absorption models are not suitable for reactive scrubbing process.

2-3 Chemical absorption

When a scrubbing solution contains a compound B, which can react with A, the contaminant in gas phase, it is refer as chemical absorption. The compound will prevent the concentration of A to build up in the bulk liquid. The overall rate expression for the reaction will have to account for the mass transfer resistance (to bring reactants together) and the resistance of the chemical reaction step. Since the relative magnitude of these two resistances can vary greatly, we have a whole spectrum of possibilities, and since each situation requires its own analysis. our first problem is to identify these kinetic regimes and to select the one which matches the given physical situation.

Depending on the relative rates of diffusion and reaction the absorption systems are classified into five different regions (Levenspiel, 1972).

* Case A: Instantaneous reaction with respect to mass transfer. Consider an infinitely fast reaction of any order:

$$aA_{(\text{from gas})} + bB_{(\text{liquid})} \text{----->} \text{ product}$$

We have

$$-r''_A = -\frac{1}{S}\frac{dN_A}{dt} = \frac{\frac{\mathscr{D}_{Bl}}{\mathscr{D}_{Al}}\frac{C_B}{b} + \frac{p_A}{H_A}}{\frac{1}{H_A k_{Ag}} + \frac{1}{k_{Al}}}$$

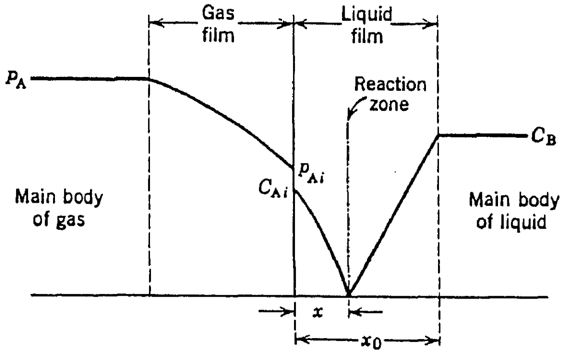
If C_a is not too high, We have the situation shown in Figure 3.

* Case B: For fast second order reaction rate between A and B, the rate expression can be written as follows:

Where $E = \frac{\sqrt{\mathscr{D}_{Al} k C_B}}{k_{Al}} = \frac{\sqrt{\mathscr{D}_{Al} k_1}}{k_{Al}}$

$$-r''_A = \frac{1}{\underset{\text{gas film}}{\frac{1}{k_{Ag}}} + \underset{\text{liquid film}}{\frac{H_A}{k_{Al}E}}}\, p_A$$

Figure 3. Concentrations of Reactants for An Infinitely Fast Irreversible Reaction (Levenspiel, 1972)



* Case C: Intermediate Rate with respect to mass transfer. These cases represent the general situation where reaction occurs both within thin film and within the main body of liquid. The general rate expressions for this regime have not been determined.

For our purposes, it suffice to note that the rate is dependant on both interfacial surface and on volume of liquid, thus the ratio

$$a_i = \frac{s}{v}$$

Where s is interfacial surface

v is the volume of liquid

becomes a parameter in this regime.

* Case D: Slow reaction with respect to mass transfer. Here the two films and main body of liquid act as resistances in series, thus we may combining and eliminating intermediate concentrations and produce the rate expression as follows (Levenspiel, 1972):

$$-\frac{1}{S}\frac{dN_A}{dt} = \frac{1}{\dfrac{1}{k_{Ag}} + \dfrac{H_A}{k_{Al}} + \dfrac{H_A a_i}{kC_B}} p_A$$

$$-\frac{1}{V_l}\frac{dN_A}{dt} = \frac{1}{\underset{\substack{\text{gas}\\ \text{film}}}{\dfrac{1}{k_{Ag}a_i}} + \underset{\substack{\text{liquid}\\ \text{film}}}{\dfrac{H_A}{k_{Al}a_i}} + \underset{\substack{\text{bulk}\\ \text{liquid}}}{\dfrac{H_A}{kC_B}}} p_A$$

* Case E: Infinitely slow reaction: Here the mass transfer resistance is negligible, the composition of A and B are uniform in the liquid, and the rate is determined by chemical kinetics only. The rate can be given directly by

$$-r_{A,l} = -\frac{1}{V}\frac{dN_A}{dt} = kC_AC_B$$

Usually cases A and B describe gas scrubbing process for air pollution control.

2-4 Controlling factor determination

Absorption is classified into physical and chemical absorptions. Since there is no reaction in physical absorption, it is controlled by solubility while either chemical reaction or diffusion may control a chemical absorption.

2-4-1 Physical absorption controlling factor determination

The value of Henry's Law constant and the relation between the overall, gas phase and liquid phase mass transfer coefficients can be used to determine which phase controls the rate of mass transfer in a physical absorption process.

The gas phase resistance is controlling when the gas is highly soluble. This means that there is virtually no resistance in absorbing the gas once it reaches the liquid interface. A high solubility also implies a high diffusion rate in the liquid phase. Therefore the rate controlling step must either be gas phase diffusion or the resistance associated with crossing the interface. Since the two film theory assume that there is no resistance at the interface, the gas phase diffusion is the controlling factor in this case.

The opposite situation occurs when one component has limited solubility in the liquid phase. There is resistance to disolution. The diffusion in the liquid will be low. As the gas phase maintains a nearly saturated interface, the mass transfer rate depends on the rate at which the solute can be removed from the interface. In this case, the local and liquid film coefficients for mass transfer are approximately the same.

If the value of the Henry's law constant is < 0.187 atm. l/g.mole, the gas phase controls the rate of mass transfer. If $H > 187.3$ atm.l/g.mole, the liquid phase is controlling.

Another way to determine which phase offers the most resistance is to examine the ratio of the local and overall mass transfer coefficients. If $K_g/K_{og} < 2$, the gas phase probably controls. If this is < 1.1, the gas phase definitely controls. If the ratio is high,about 10, the liquid phase is controlling (Bethea, 1978).

As a general rule, gas phase diffusion is much faster than liquid phase diffusion and thus governs the type and size of the absorption equipment selected for any particular application.

2-4-2 Chemical absorption controlling factor determination

To determine whether a reaction is fast or slow, we focus on unit surface of gas-liquid interface. we assume that gas phase resistance is negligible and we define a film conversion parameter (Levenspiel, 1972):

$$M = \frac{\text{maximum possible conversion in film}}{\text{maximum diffusion transport through film}}$$

$$= \frac{kC_{Ai}C_{B}x_{0}}{\frac{\mathscr{D}_{Al}}{x_{0}} \cdot C_{Al}} = \frac{kC_{B}\mathscr{D}_{Al}}{k_{Al}{}^{2}}$$

If M >>1 all reaction occurs in the film, and surface area is the rate controlling factor. On the other hand, if M << 1, no reaction occurs in the film, and bulk volume becomes the rate controlling factor. More precisely, it has been found that:

A) If M > 4, reaction occurs in the film and we have cases A and B in previous section.

B) If 0.0004 < M < 4, we then have the intermediate cases, C and D.

C) If M< 0.0004, we have the infinitely slow reaction of case E.

For process design, when M is large, a contecting device is chosen which develops or creates large interfacial area, energy for agitation is usually an important consideration. On the other hand, If M is very small, all we need is a large volume of liquid.

3 A LITERATURE REVIEW OF NO ABSORPTION

The removal of NO_x from flue gases has received considerable attention due to federal regulations associated with the "Clean Air Act". the absorption of NO_x from flue gases is very complex because:

a) The NO_x gas is a mixture of several components consisting primarily of NO and NO_2 but could contain trace amounts of N_2O N_2O_3 N_2O_4 and N_2O_5.

b) More than forty equilibrium reactions may be needed to explain the chemistry between nitrogen oxides and oxyacids.

c) Absorption and desorption operations occur simultaneously.

d) All kinds of complex reactions occur in this system.

e) Needed physical-chemical data is generally not available.

During the past fifty years, much data have been published in various aspects of NO_x absorption. Much of these data were compiled in order to define areas for the future research.

3-1 Equilibrium

In the absorption of NO_x gas in aqueous solutions, every component in the system takes part in one or more reaction with other components. Equilibria occur in the gas as well as in the liquid phase. In the following section, this type of information will be reviewed.

3-1-1 Gas phase equilibrium

The following equilibria occurs in the gas phase:

$$2\ NO_2(g) \xleftrightarrow{K_1} N_2O_4(g)$$

$$NO(g) + NO_2(g) \xleftrightarrow{K_2} N_2O_3(g)$$

$$NO(g) + NO_2(g) + H_2O(g) \xleftrightarrow{K_3} 2\ HNO_2(g)$$

Where K_1, K_2 and K_3 are the pressure based equilibrium constants of each reaction. The K_1 value is given by the following equation (Bronsted, 1922; JANAF 1971):

$$\log K_1 = \frac{2993}{T} - 11.232$$

In SI unit $(kPa)^{-1}$. and T in K.

The K_2 value is given by (Beattie, 1963; Beattie and Bell, 1947):

$$\log K_2 = \frac{2072}{T} - 9.240 \quad (kPa)^{-1}$$

The value of K_3 reported by Wayne and Yost (1951); Waldorf and Babb (1964); Ashmore and Tyler (1961) and Karavev (1962) is $1.4*10^{-2}$. at 25°C. However, the NBS (1968) and JANAF (1971) compilations give the values of 1.7 and 0.194 kPa^{-1} respectively. Schwartz and White (1981) analyzed the published literature and they compiled the data on standard free energies of formation summarized in Table 5.

Table 5 Standard Free Energies and Enthalpies of Formation at 298 K

Species	Standard Free Energy of Formation kJ/kmole × 10^{-3}	Standard Enthalpy of Formation kJ/kmole × 10^{-3}
NO_2	51.32	33.19
NO	86.61	90.29
N_2O_3	139.48	83.76
N_2O_4	97.87	9.17
N_2O_5	115.12	11.30
HNO_3	−74.18	135.12
HNO_2	−46.05	−79.53
$H_2O(g)$	−228.70	−241.934
$H_2O(l)$	−237.292	−285.967

3-1-2 Aqueous phase equilibria

Aqueous phase equilibria can be written in terms of gas phase and mixed phase equilibria. Consider the following reactions:

$$2\ NO_2(g) + H_2O\ (l) \overset{K_4}{\longleftrightarrow} HNO_2(aq) + NO_3^-(aq) + H^+(aq)$$

$$NO(g) + NO_2(g) + H_2O \overset{K_5}{\longleftrightarrow} 2\ HNO_2(aq)$$

$$2\ NO(g) \overset{K_6}{\longleftrightarrow} 2\ NO(aq)$$

These equations give:

$$3\ HNO2(aq) \overset{K_{a1}}{\longleftrightarrow} H^+(aq) + NO_3^-(aq) + 2\ NO(aq) + H_2O(l)$$

$$\text{Where } K_{a1} = \frac{K_4}{(k_5)^2} H_{NO}^2$$

$$2\ NO_{2(1)} \xleftrightarrow{K_{a2}} 2\ H^+ + NO_2^- + NO_3^-$$

$$\text{Where } k_{a2} = \frac{K_4}{H_{NO2}^2}$$

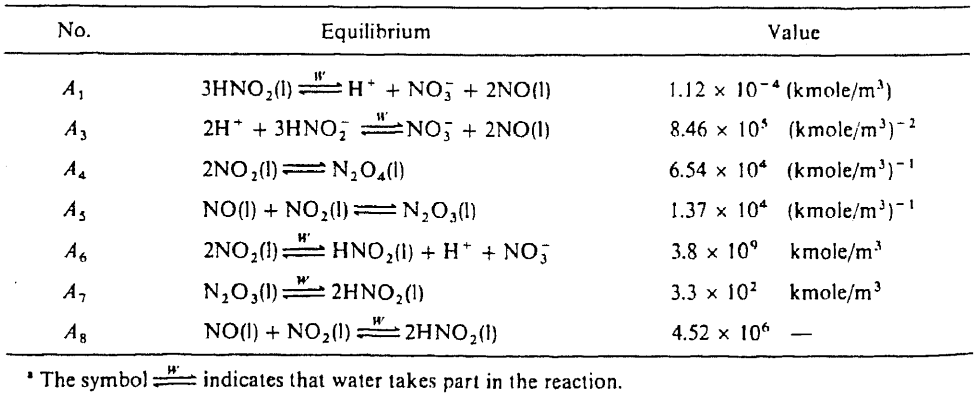
Schwartz and White (1981) reviewed the experimental data on liquid phase equilibrium. The result are summarized in Table 6. The symbol w in equations indicates that water take part in these reactions.

3-1-3 Solubility

(A) Nitric oxide (NO)

Solubility of nitric oxide in water with respect to temperature has been reported in International Critical Tables

Table 6 Aqueous phase equilibria



No.	Equilibrium	Value
A_1	$3HNO_2(l) \xrightleftharpoons{w} H^+ + NO_3^- + 2NO(l)$	1.12×10^{-4} (kmole/m^3)
A_3	$2H^+ + 3HNO_2^- \xrightleftharpoons{w} NO_3^- + 2NO(l)$	8.46×10^5 (kmole/m^3)$^{-2}$
A_4	$2NO_2(l) \rightleftharpoons N_2O_4(l)$	6.54×10^4 (kmole/m^3)$^{-1}$
A_5	$NO(l) + NO_2(l) \rightleftharpoons N_2O_3(l)$	1.37×10^4 (kmole/m^3)$^{-1}$
A_6	$2NO_2(l) \xrightleftharpoons{w} HNO_2(l) + H^+ + NO_3^-$	3.8×10^9 kmole/m^3
A_7	$N_2O_3(l) \xrightleftharpoons{w} 2HNO_2(l)$	3.3×10^2 kmole/m^3
A_8	$NO(l) + NO_2(l) \xrightleftharpoons{w} 2HNO_2(l)$	4.52×10^6 —

[a] The symbol $\xrightleftharpoons{w}$ indicates that water takes part in the reaction.

(1928), Handbook of Chemistry and Physics (1963) and by Seidell and Linke (1965). The value of Henry's law constant can be correlated by the following equation

$$\log H_{NO} = \frac{-1463.32}{T} + 2.178$$

Where H_{NO} is in kg mole/m^3 atm.

Armor (1974) has measured the solubility of NO as a function of pH (2-13). He has shown that, in the pH range studied, there was no change in the value of the solubility.

The solubility of NO in aqueous electrolyte solutions can be calculated by using the following equation

$$\log \left(\frac{H}{H_w}\right) = -\sum K_s * I$$

Where H and H_w are the values of solubility in the solution and water, respectively. K_s is the salting out parameter and is given by the following equation

$$K_s = i^+ + i^- + i_g$$

Where i^+ , i^- are the contributions of the cations and anions of the electrolyte and i_g is the contribution of the solute gas. Danckwerts (1970) reported the values of i^+ and i^- for various cations and anions. On the basis of these values and the solubility data reported by Armor (1974) the value of i_g

for NO is 0.037 m^3/k ion.

(B) Nitrogen dioxide (NO_2)

The determination of solubility of NO_2 in water is difficult because NO_2 reacts with water. Andrew and Hanson (1961) and Komigama and Inoue (1980) found the solubility of NO_2 in water using the theory of absorption followed by pseudo nth order chemical reaction. The value of Henry's law constant was found to be 0.04 at 25°C [Andrew and Hanson] and 0.024 at 15°C [Komiyama and Inoue]. This method needs the knowledge of diffusivity (D) of NO_2 in water and the reaction rate constant (k) between disolved NO_2 and water.

Garcdel et al., (1975) obtained a preliminary estimate of Henry's law constant of NO_2 on the basis of following equation

$$\frac{H_{NO2}}{H_{NO}} = \frac{H_{CO2}}{H_{CO}}$$

The value H_{NO2} works out to be 0.07 (kgmole/ m^3 atm) at 25°C. Schwartz and White (1981) have correlated the solubilities of gases with their boiling points. Using this relation the value of H_{NO2} = 0.02 was estimated at 25°C.

3-2 Absorption of NO followed by oxidation

Oxidation of NO is the most important step in the NO scrubbing process. Oxidation of NO to NO_2 is relatively slow, and thus, becomes the rate limiting step in most approaches. Further more, chemical oxidation of NO is required when its concentration is very small. The common agents include; nitric acid, ozone, hydrogen peroxide, chlorine dioxide, chlorite, etc.

(A) Ozone

The reaction of NO with ozone is given by the following equation

$$NO + O_3 \text{ ----> } NO_2 + O_2$$

The resulting nitrogen dioxide can conveniently be scrubbed in caustic solutions even at low ppm values. The mechanism of above reaction has been studied by Harcourt (1972) and Bhatia and Hall (1980). The kinetics has been investigated by Borders (1982).

(B) Sulfuric acid

Topol, et al., (1968) used sulfuric acid as the oxidizing agent. The reaction is represents by:

$$4\ NO + 3\ H_2SO_4 \text{ <----> } 2\ NO^+ +2\ NO_2 + H_3O^+ + 3\ HSO_4^-$$

$$2\ NO + 5\ H_2SO_4 \text{ <----> } 2\ NO^+ + SO_2 + 2\ H_3O^+ + 4\ HSO_4^-$$

The equilibrium constant values of the first and second reactions were found to be $2*10^{50}$ $(kgmole/m^3)^3$ and $4*10^{12}$ $(kgmole/m^3)^7$, respectively. The rate of the second reaction was second order in NO and the rate constant was found to be 0.2 (m^3/kgmole s).

(C) Hydrogen peroxide

Takahashi et al., (1979) carried out gas phase NO oxidation using hydrogen peroxide. Nitric oxide and hydrogen peroxide were taken in the ratio of 1 : 13 at a temperature more than 400^o C and using 100 ppm NO. The extent of NO oxidation was greater than 95%. Absorption experiments were carried out using 101.5 mm ID stirred cell by Lodhabhoy and Sharma (1969). The reaction between NO and H_2O_2 is given by the following equation

$$NO + H_2O_2 \longleftrightarrow NO_2 + H_2O$$

Absorption of NO is accompanied by fast pseudo first order chemical reaction. The value of reaction rate constant at 30 ^oC was found to be $8.42*10^2$ (m^3/kgmole s) with an activation energy of 13,700 kcal/kg mole.

(D) Potassium permanganate

Potassium permanganate was used for the oxidation of NO by Kann et al., (1976). Conversion of NO exceeding 80% has been reported. Sada et al., (1977) studied the oxidation of NO using aqueous solutions of $KMnO_4$ and aqueous solutions mixed solutions of $KMnO_4$ and NaOH.

In the absence of NaOH the reaction between NO and $KMnO_4$ can be represented by the following equation:

$$NO + MnO_4^- \longrightarrow NO_3^- + MnO_2(s)$$

Uchida et al., (1983) showed that the product of reaction with MnO_2 has some inhibiting effect on the rate of reaction.

In the presence of NaOH, the oxidation reaction enhances the reaction between NO and $KMnO_4$ in a strong aqueous caustic solution is given by

$$NO + MnO_4^- + 2\ OH^- \longrightarrow NO_2^- + MnO_4^{-2} + H_2O$$

Similiar observation has been reported by Teramoto et al., (1969).

(E) Sodium chlorite

The absorption of NO in aqueous mixed solutions of $NaClO_2$ and NaOH has been studied by Teramoto et al., (1976) and Sada et al., (1978, 1979). Oxidation of NO with $NaClO_2$ in the presence of NaOH can be presented by

$$4\ NO + 3\ ClO_2^- + 4\ OH^- \longrightarrow 4\ NO_3^- + 3\ Cl^- + 2\ H_2O$$

The rate constant decreases with an increase in the concentration of NaOH.

(F) Chlorine dioxide

Two Japanese patents claim the use of chlorine dioxide for NO oxidation (Kushiro, et al., 1976 and Hayashi et al., 1976) The process was applied the removal of NO from flue gas. The conversion with respect to NO has been claimed to be about 90%.

(G) Sodium sulfite

Takeuchi, et al., (1977a, 1977b, 1978) have studied the absorption of NO in aqueous solutions of sodium sulfite at 25°C. The absorption of NO in Na_2SO_3 solution was accompanied by a fast pseudo second order reaction with respect to NO and zero order in sulfite.

Uchida, et al., (1983) studied NO absorption which initially increases with Na_2SO_3 concentration, attains a maxima when $[Na_2SO_3]$ is 0.1 k mole/m^3 and then decreases.

(H) Sodium dithionite

Lahari (1981) measured specific rates of absorption of NO in aqueous caustic solutions of sodium dithionite ($Na_2S_2O_4$) and sodium sulfide (Na_2S) at 31°C and 27°C respectly. The reaction between NO and aqueous caustic solution of $Na_2S_2O_4$ was found to be first order with respect to NO only. The first order rate constant was found to be $2.3*10^3$ s^{-1} at 31°C. The reaction between NO and the caustic aqueous solution of sodium sulfide was found to be zero order in Na_2S and zero order in NO. The rate constant was found to be $1.69*10^{-4}$ kgmole/m^3 s at 27°C.

3-3 Absorption of NO followed by complex reaction

(A) $FeSO_4$

Kustin, et al., (1966) have reported that the NO absorption into $FeSO_4$ solution is an equilibrium reaction

$$NO + FeSO_4 \longleftrightarrow Fe(NO)SO_4$$

The forward reaction was found to be first order in both NO and $FeSO_4$. The reverse reaction was found to be first order with respect to the complex $Fe(NO)SO_4$. Similar observations have been reported by Hikita, et al., (1977). The value of second order rate constant for the forward reaction was given by the following equation:

$$\log (k_2)_{NO} = 10.303 + 0.124\ I - \frac{1337}{T}$$

Where I is the ionic strength.

(B) Fe^3-EDTA

The absorption of NO in aqueous solution of Fe^3-EDTA and aqueous slurries of $MgSO_3$ with Fe^2-EDTA was carried out by Sada, et al., (1981). The the forward complexing reaction was represented by:

$$NO + Fe^3\text{-EDTA} \text{ ----> } Fe^3\text{-(NO)(EDTA)}$$

The reaction was found to be first order in NO and 1.5 order in Fe^3-EDTA at pH of 7.0.

(C) Na_2SO_3/Fe^3-EDTA-Na

Hikita, et al., (1978) performed a series of experiments for the NO absorption into Na_2SO_3/Fe^3-EDTA-Na solution. The rate constants are independent of Na_2SO_3 concentration and dependent on Fe^3-EDTA-Na, ionic strength of present and the temperature.

(D) Ferrous cysteine

The absorption of NO in Ferrous cysteine aqueous solution was reported by Shih-Ger Chang et al., (1988). The advantage over the conventional Fe^{+2}-EDTA system is cysteine can be regenerated. The best regeneration result were obtained from the reaction of CYS-CYS with H_2S and SO_2 at pH of 10.0 and 60°C.

4 EXPERIMENTAL PROGRAM

The laboratory apparatus, chemicals and gases used to conduct the experimental program of this thesis are described in this section.

4-1 Apparatus

The basic scrubbing apparatus consists of a flue gas blending system, a matched pair of gas scrubbers and an analytical train. The blending system is capable of producing a mixture of nitrogen, oxygen, nitric oxide and nitrogen dioxide in order to simulate a wide variety of flue gas compositions by mixing pure gases components and blends in different proportions. The synthetic flue gas was introduced into the scrubber through a polyethylene sparger. The effluent gases were carried to the gas analyzers for the determination of residual NO, NO_2 and O_2. The scrubber consists of a 5.1 cm diameter by 61 cm long pyrex pipe capped on both ends with 0.63 cm entrance and exit polyethylene tubes. The components of the scrubbing system are described in detail below.

4-1-1 Flue gas blending system

The flue gas blending system is designed to provide synthetic flue gas from high pressure gas cylinders. The blending system is constructed out of 0.63 cm diameter (O.D.) by 60 cm long stainless steel type 316 tubing. Each component gas is delivered through a 0.32 cm (O.D.) teflon tubing to a calibrated rotameter to the blending mainfold. The total flow rate from the blending system ranged from 8.9 to 0.4 standard liters per minute. Figure 4 presents the schematic of the gas blending system.

4-1-2 Scrubbing vessels

The flue gas scrubbers are 5.1 cm in diameter by 61 cm long Pyrex glass columns with a polyethylene sparger located at the botton. The flue gas was introduced into the scrubbing solution through the sparger. Figure 5 contains a schematic of the scrubber design. Two scrubbing units are available, Either one could be used as the main scrubber while the other would be the reference scrubber.

One liter of scrubbing solution is generally used to run these experiments as semibatch process with continuous (1 l/min) flue gas injection. The actual scrubbing volume was varied as the flow rate in a few experiments. The exiting gas was carried to an oxygen monitor and NO_x analyzer from the top of the glass column by 0.32 cm polyethelene tubing after removal of moisture. Liquid samples were removed periodically through a valve at the botton of the glass column to measure solution pH. The same solution was then injected in a Dionex Ion chromatograph to measure the anion concentrations of reactant (ClO_2^-) and products (Cl^- and NO_3^-).

Figure 4 Schematic of the Gas Blending System

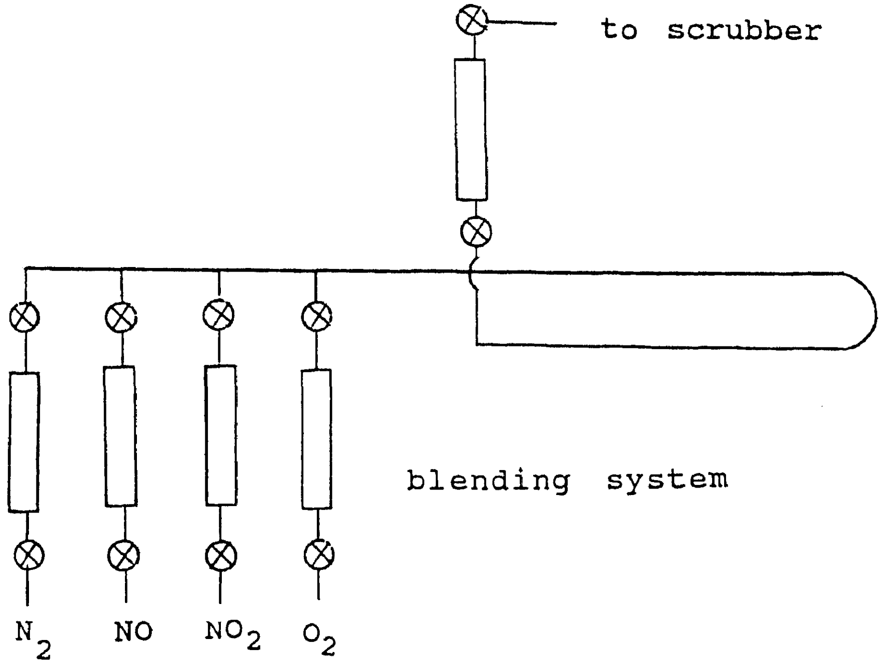
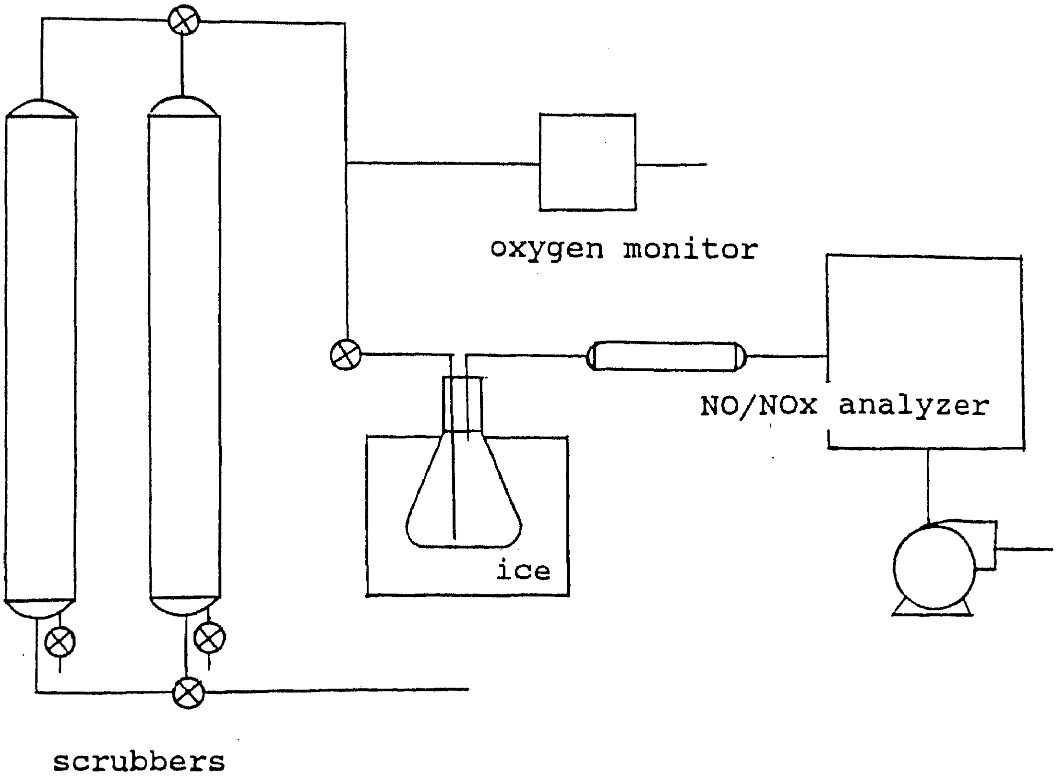


Figure 5 Schematic of Scrubber Design



When conducting a scrubbing experiment, the following sequence was followed:

- * Set the flue gas composition and flow rate while flowing through the reference scrubber.
- * Switch flue gas through the main scrubber (prefilled with the desire solution).
- * Monitor pH and temperature.
- * Check inlet flue gas composition using the oxygen monitor and NO_x analyzer.
- * Measure outlet composition as a function of run time.
- * Take liquid sample periodically.
- * Run liquid sample in ion chromatography.

4-2 Reagents

$NaClO_2$ and NaOH were used as the NO oxidizer and NO_2 neutralizer in the scrubber. The synthetic flue gas was produced by mixing NO, NO_2 and O_2 gases from high pressure gas cylinders with nitrogen making up the balance. The source and purity of these chemicals are discussed below.

4-2-1 Sodium chlorite

Commercial sodium chlorite containing approximately 80% $NaClO_2$, 18% Na_2CO_3 and 2% Na_2SO_4 was supplied by Pfaltz & Bauer inc. Waterburg, CT 06708.

Textone is the commercial name of sodium chlorite, which is prepared by the reaction of a reducing agent on chlorine dioxide in an alkaline medium.

Sodium chlorite is the sodium salt of the unstable chlorous acid, having a dissociation constant of $K_a = 0.01$. The salt exists both in anhydrous and a trihydrated form. The crystals of $NaClO_2$ are white, but they usually have a greenish tint because traces of chlorine dioxide are present. The chlorite anion is more stable than hypochlorite anion, but less stable than chlorate anion. In cold alkaline solutions, sodium chlorite has only mild oxidizing power. However, heating or acidification, or both, make chlorite solutions strongly oxidizing. Due to the strong oxidizing risk, sodium chlorite should never be stored in open containers.

4-2-2 Sodium hydroxide

Commercial sodium hydroxide (caustic soda, sodium hydride, lye, white caustic) NaOH was supplied by Pfaltz & Bauer, Inc. CT. 06708. It is a white deliquescent solid, absorbs water and carbon dioxide from the air. Its melting point is 318°C, boiling point is 1390°C. At normal condition, it disolves in water, alcohol, and glycerol.

Sodium hydroxide is corrosive to tissue in presence of moisture: strong irritant to tissue (eyes, skin, mucous membranes). Its tolerance amount is 2 mg per cubic meter of air.

4-2-3 Gases

A) Nitric Oxide:

The nitric oxide was supplied as a 10% blend by

Union Carbide Corporation
Linde Division
National Specialty Gases Office
100 Davidson avenue
Somerset, NJ 08873

By the following order informations and specifications

Cylinder type: T
Grade: custom blend
Concentration: 10% NO in nitrogen
Volume: 6.79 m^3
Cylinder pressure: 14,824 kpa.
Regulator used: UPG-CGA 160/660 in stainless steel

Nitric oxide is a colorless gas, which is slightly soluble in water and noncombustible. It usually used to prepare nitrosyl carbonyl.

It is highly toxic by inhalation; strong irritant to skin and mucous membrances; supports combustion. Its tolerance concentration is 25 ppm in air.

B) Nitrogen Dioxide:

The nitrogen dioxide mixed cylinder was supplied as a 0.5% blend by Union carbide corporation, Linde Division. by the following order informations and specifications:

Cylinder type: T

Grade: custom blend

Concentration: 0.5% NO_2 in Nitrogen.

Volume: 6.79 m^3

Cylinder pressure: 14,824 kpa

Regulator used: UPG-CGA 160/660, stainless steel

Nitrogen dioxide is a red-brown gas or yellow liquid; becomes colorless solid at -11.2°C, which exists in varying equilibrium with other oxides of nitrogen as the temperature is varied.

Nitrogen dioxide is used in the production of nitric acid, nitrating agent, oxidizing agent, catalyst, oxidizer for rocket fuel, and polymerization inhibitor for acrylates.

NO_2 has been found to be very toxic, inhalation may be fatal. Its tolerance concentration is 5 ppm.

C) Oxygen:

The pure oxygen cylinder was supplied by Union Carbide Corporation, Linde Division by the following order informations and specifications

Cylinder type: T.

Grade: extra dry.

Minimum purity: 99.6%

Maximum moisture 10 ppm

Volume: 7.05 m^3

Weight: 69.5 kg

Cylinder pressure: 15,168 kpa

Regulator used: UPE-CGA 540 brass

Oxygen is a colorless, odorless, tasteless diatomic gas. It is actually a noncombustion gas, but actively supports combustion and may explode on contect with heat oxidizable material. High concentration oxygen also irritant to skin and tissue.

D) Nitrogen:

The nitrogen gas cylinder was supplied by Union Carbide Corporation, Linde Division. by the following order informations and specifications

Cylinder type: T
Grade: prepurified
Minimum purity: 99.998%
$H_2O < 3$ ppm
$O_2 < 5$ ppm
volume: 6.46 m^3
Weight: 67.7 kg
Cylinder pressure: 15,168 kpa
Regulator used: UPE-CGA 580 brass

Nitrogen is a colorless, tasteless diatomic gas consitituting about four fifths of the air. The gas is noncombustible and slightly soluble in water and alcohol.

4-3 Analysis

Concentration changes were obtained by a train of analytical instruments. They are

* Chemiluminescent NO/NO_x analyzer

  Model 10 A

  Thermoelectron Instruments Inc.

* Beckman NO/NO_x analyzer

  Model 955

  Beckman Industrial Corp.

* Process oxygen monitor

  Model 715

  Beckman Industrial Corp.

* Beckman oxygen monitor

  Model 7005

  Beckman Industrial Corp.

* pH meter

  Model 6071

  Jenco Electronic LTD.

* Ion chromatography

  System 2120i

  Dionex Corporation

4-3-1 Flue gas analysis

The outlet line carrying the scrubber effluent entered a junction from which two lines exited. These lines deliver the effluent to the analyzers for measurement of the concentrations of NO, NO_2 and O_2.

The Thermoelectron NO_x analyzer is used to measure the concentration of NO and NO_2. This instrument make use of the chemiluminescent properties of the NO reaction with ozone as a measure of NO concentration. NO molecules are mixed with O_3 from the ozone generator and carried into a reaction chamber where NO is electronically converted to excited NO_2. Excited NO_2 than emit light (Chemiluminescence).

$$NO + O_3 \text{ ----> } NO_2^* + O_2$$

$$NO_2^* \text{ ----> } NO_2 + hv$$

The basic chemiluminescent analyzer is only sensitive to NO molecules. NO_2 is measured by thermally converting the NO_2 to NO and measuring the incremental increase in concentration of NO. A temperature controller is used to maintain the proper temperature for NO_2 reduction. The proper temperature is 650°C.

Both concentrations of NO and NO_2 were analyzed by a Beckman 955 NO/NOx analyzer independently to double check the results.

Both instruments were calibrated with a analyzed mixture of 100 ppm NO and 109 ppm NO_2 in nitrogen. In all runs, the agreement between both measurements are better than 10%. The output signal from both analyzers were continuously recorded.

The oxygen concentration is determined with a Beckman model 715 process oxygen monitor. This instrument has an amperometric oxygen sensor, which contains a metallic cathode and anode. The two electrodes are separately mounted within the polypropylene body and are electrically connected by a potassium chloride electrolyte. A constant potential is impressed across the two electrodes.

A gas-permeable teflon membrane separates the electrodes from the process sample and fits firmly against the cathode. Oxygen from the sample diffuses through the membrance and is reduced at the cathode. The resultant electrical current flow between the anode and cathod is proportional to the partial pressure of oxygen in the sample.

The sensor is calibrated with an analyzed 5% oxygen in nitrogen mixture and an air sample assumed to be 21% oxygen. Signal from the monitor is recorded continuously.

A Beckman model 7005 oxygen monitor is used to double check the result from model 715. The agreement between these two instruments is always better than 10%.

4-3-2 Scrubbing solution analysis

A Jenco 6071 pH meter was used to measure the pH value and temperature of the scrubbing solution. Janco 6071 is a microcomputer based pH/mv/temperature meter with following specifications:

* Range

  pH: -2.00 to 16.00

  Temperature: 0 to 100^{o}C

  mV: -999 to 999

* Resolution

pH: 0.01

Temperature: 0.1

mV: 1.0

* Accuracy

pH: 0.1%

Temperature: 0.5%

mV: 0.1%

Liquid samples were taken from the scrubber at regular time interval. Ionic concentrations were determined both qualitatively and quantitatively using Dionex ion chromatography system 2120i under the following conditions:

Column: BIO-RAD
IC-anion-PW
Catalogue-127-0062
Serio # 10825

Flow rate: 1.2 ml/min

Low pressure limit: 0 psi

High pressure limit: 700 psi

Temperature compensation: 1.7

Output range: 30 us

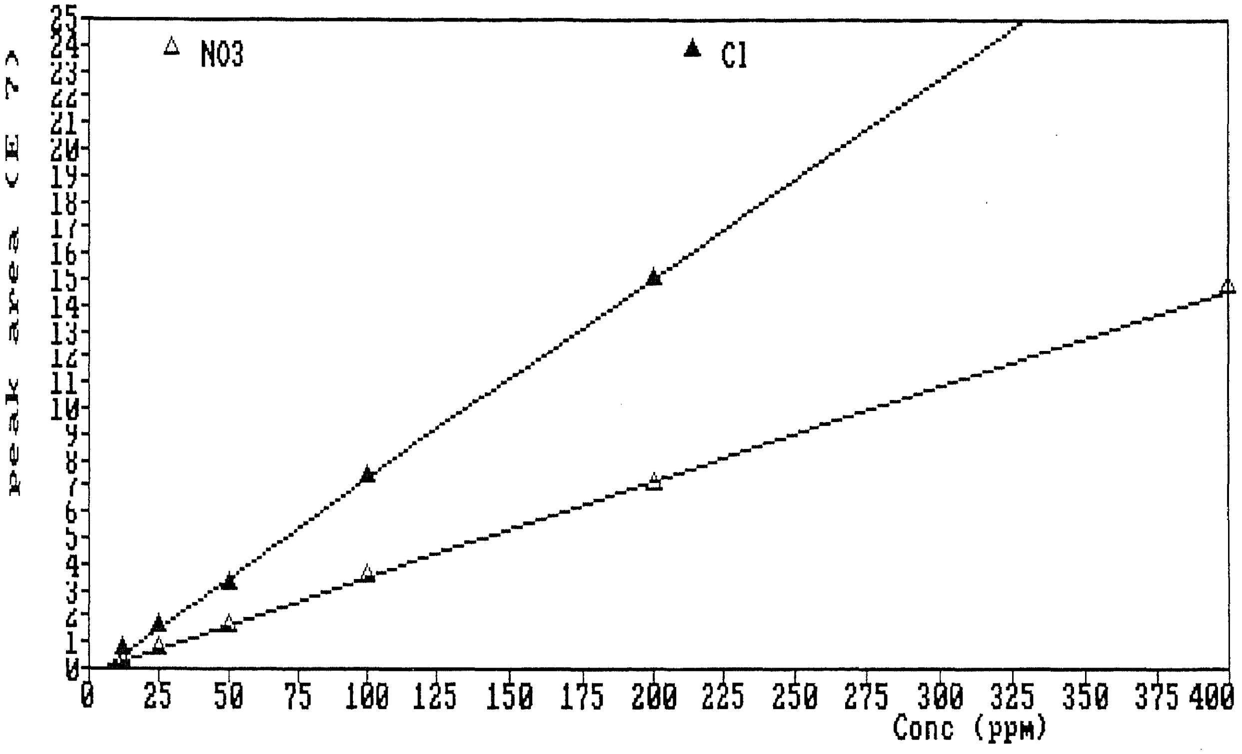
The sample injection is pushed by buffer eluent through the analytical column, where ions are separated. After separation, the sample is carried to a conductivity detector, which is based upon the electrical conductivity of the sample when placed between two oppositely charge electrodes. The presence of ions in the solution allows electrical current to flow between the electrodes, completing the circuit. At low concentrations, conductivity is directly proportional to the concentration of conductive species in the solution. The total ionic concentration of the solution in the cell and the temperature of that solution affect the linearity of this relationship.

Table 7 contains data on a series of standard at varies concentrations. Figure 6 is the peak area-concentration calibration curve of Cl^- and $NO3^-$, using this curve, concentrations of Cl^- and NO_3^- can be obtained.

Table 7 Peak Area-Concentration Data of Cl^- and NO_3^- of Dionex IC Systen 2120i

conc. ppm.	species anion	peak area 10^7
400	Cl^-	26.52
	NO_3^-	14.65
200	Cl^-	15.05
	NO_3^-	7.08
100	Cl^-	7.33
	NO_3^-	3.52
50	Cl^-	3.20
	NO_3^-	1.61
25	Cl^-	1.58
	NO_3^-	0.80
12.5	Cl^-	0.69
	NO_3^-	0.25

Figure 6 Relationship Between Peak Area and Concentration of Cl^- and NO_3^- of Dionex IC System 2120i



5 RESULTS

An aqueous scrubbing program was conducted to test sodium chlorite as an in situ oxidizer to absorb NO by means of oxidation and absorption in an alkaline solution from a gas stream that simulates the composition of incineration emission.

The objective of the scrubbing tests were to:

* Determine the potential of $NaClO_2$ aqueous scrubbing for NO oxidation and absorption.
* Obtain the rate parameters for NO oxidation to NO_2 by $NaClO_2$.

Experiments are detailed in the following sections.

5-1 Absorption of NO in Caustic Aqueous Scrubbing

A series of runs of aqueous scrubing of flue gas containing NO of 300, 500, and 800 ppm in N_2 had been performed at following conditions

Flue gas:

NO: 300, 500, 800 ppm
Balance: N_2
Flow rate: 1 l/min

Scrubbing solutions:

NaOH: 0, 0.0001, 0.01, 1.0 M
Volume: 1 liter

All tests were conducted at room temperature (25°C) and atmospheric pressure.

Results contained in Table 8 indicate that NO can not be absorbed by distilled water. Similarly, the presence of NaOH up to 1.0 M did not improve the NO absorption.

Table 8 Absorption of NO in Caustic Aqueous Scrubbing

NO (ppm)	Expt	absorption %			
		Conc. of NaOH (molarity)			
	#	0	0.0001	0.1	1
300	1	0.3	0.8	0.7	0.6
	2	0.4	1.3	1.1	1.2
	3	0.7	1.1	0.3	1.3
	avg	0.5	1.1	0.7	1.0
500	1	0.8	1.8	1.7	0.7
	2	0.3	0.9	0.9	0.8
	3	1.1	0.6	0.3	1.0
	avg	0.7	1.1	1.0	0.8
800	1	0.7	2.1	0.6	0.7
	2	0.4	1.1	0.0	1.4
	3	0.6	0.4	1.7	1.2
	avg	0.6	1.2	0.8	1.1

$$\text{Absorption } \% = 1 - \frac{\text{NO(out)}}{\text{NO (in)}} * 100\%$$

5-2 Absorption of NO_2 in Caustic Aqueous Scrubbing

A number of experiments were carried out to test the absorption of NO_2 in caustic aqueous scrubbing. which were conducted at the following conditions

Flue gas:

NO_2: 300, 500, 800 ppm
Balance: N_2
Flow rate: 1 l/min

Scrubbing solutions:

NaOH: 0.01, 0.1, 0.5 M
Volume: 1 liter

The experiments were conducted at room temperature and pressure.

Data in Table 9 show that NO_2 can be effectively absorbed by NaOH solution. Runs with 0.5 M NaOH indicated that absorption of more than 98% is achieved.

Table 9 Absorption of NO_2 in Caustic Aqueous Scrubbing

NO_2	Expt	absorption %		
		Conc. of NaOH (molarity)		
(ppm)	#	0.01	0.1	0.5
300	1	74.0	76.4	95.9
	2	73.3	72.5	96.6
	3	72.8	72.4	96.2
	avg	73.4	73.8	96.6
500	1	80.0	84.4	97.2
	2	80.8	81.8	97.4
	3	80.0	82.8	98.2
	avg	80.3	83.0	97.6
800	1	83.4	90.0	97.5
	2	81.4	89.1	98.6
	3	80.6	89.1	98.1
	avg	81.8	89.9	98.1

$$\text{Absorption \%} = 1 - \frac{NO_2(\text{out})}{NO_2\ (\text{in})} * 100\%$$

5-3 NO_2 effect on NO absorption in caustic aqueous scrubbing

A number of experiments were performed to evaluate the effect of the reaction

$$NO + NO_2 \text{ <----> } N_2O_3$$

$$N_2O_3 + H_2O \text{ ----> } 2\ HNO_2$$

in caustic aqueous scrubbing. Experiments were conducted at the following conditions

Flue gas:

Equal molar of NO and NO_2 at 300, 500, 800 ppm

Balance: N_2

Flow rate: 1 l/min

Scrubbing Solutions

NaOH: 0.01, 0.5 M

Volume: 1 liter

There tests were conducted at room temperature and atmospheric pressure.

The actual measurements are summarized in Tables 10 and 11. These data indicate that the presence NO_2 significently increases NO absorption in caustic aqueous solution.

Table 10 NO_2 Effect on NO Caustic Aqueous Scrubbing

Conc. (ppm)	Expt #	NO(in) (ppm)	NO(out) (ppm)	Abs %	NO_2(in) (ppm)	NO_2(out) (ppm)	Abs %
300	1	361	136	62.3	318	5	98.4
	2	330	84	74.5	295	11	96.3
	3	325	125	61.5	352	13	96.3
	avg			66.1			97.0
500	1	568	186	67.3	568	23	96.0
	2	591	182	69.2	568	25	95.6
	3	542	167	69.2	573	22	96.2
	avg			68.6			95.9
800	1	813	333	59.0	833	17	98.0
	2	843	354	58.0	823	10	98.8
	3	813	385	52.6	875	0	100.0
	avg			56.5			98.9

* NaOH = 0.01 M

$$* \text{ Abs(NO)} = 1 - \frac{\text{NO(out)}}{\text{NO (in)}} * 100\%$$

Table 11 NO_2 Effect on NO Absorption in Caustic Aqueous Solution

Conc. ppm	Expt #	NO(in) ppm	NO(out) ppm	Abs %	NO_2(in) ppm	NO_2(out) ppm	Abs %
300	1	310	5	98.5	324	0	100
	2	355	19	94.6	324	0	100
	3	379	17	95.6	336	0	100
	avg			96.2			100
500	1	576	21	96.3	602	0	100
	2	595	14	97.6	602	0	100
	3	600	17	97.3	595	0	100
	avg			97.0			100
800	1	845	21	97.5	840	0	100
	2	867	24	97.3	893	0	100
	3	826	10	98.8	833	0	100
	avg			97.9			100

* NaOH = 0.5 M

5-4 Oxygen Effect on NO Absorption in Caustic Aqueous Scrubbing

Oxygen is generally present in incinerator emissions because excess air is used to make sure incinerator feed is completely combusted. Since oxygen react with NO to form NO_2, it is important to determine its contribution to NO absorption. the following runs were performed to test this effect.

Flue gas

NO: 300, 500, 800, 2000 ppm

O_2: 5%

Balance: N_2

Flow rate: 1 l/min

Scrubbing solutions

NaOH: 0.0001, 0.01, 1 M

Volume: 1 liter

All runs were conducted at room temperature and pressure.

Results in Table 12 indicate that no significent change in NO absorption in caustic aqueous scrubbing occurs due to introduction of 5% O_2 into synthetic flue gas.

Table 12 Effect of 5% Oxygen on NO Absorption in Caustic Aqueous Scrubbing

NO(ppm)	Expt #	absorption %		
		Conc. of NaOH (molarity)		
		0.0001	0.01	1.00
300	1	0.0	0.5	0.0
	2	1.8	0.0	1.2
	3	1.1	0.8	0.3
	avg	1.0	0.4	0.5
500	1	1.5	0.2	0.2
	2	1.9	1.1	0.1
	3	0.0	0.8	1.7
	avg	1.1	0.7	0.7
800	1	1.4	0.0	2.0
	2	0.0	1.4	0.9
	3	0.0	1.4	0.0
	avg	0.4	0.9	1.0
2000	1	1.3	0.5	1.7
	2	0.0	1.0	1.0
	3	0.4	0.4	4.5
	avg	0.6	0.6	2.4

$$\text{Absorption } \% = 1 - \frac{\text{NO(out)}}{\text{NO (in)}} * 100\%$$

5-5 Oxidation of NO by $NaClO_2$ in aqueous scrubbing

A number of experiments were performed to evaluate the potential of sodium chlorite ($NaClO_2$) to oxidize NO in aqueous scrubbing under the following conditions

Flue gas

NO: 2000 ppm
Balance: N_2
Flow rate: 1/min

Scrubbing solution

$NaClO_2$: 0.008 M
Na_2SO_4: $1.3*10^{-4}$ M
Na_2CO_3: $1.5*10^{-3}$ M
Volume: 1 liter

These runs were conducted at room temperature and pressure.

The first set of experiments was made to evaluate the oxidation and absorption of NO in $NaClO_2$ aqueous scrubbing and to ascertain the products and material balance in this reaction. Due to the impurities (18% Na_2CO_3 and 2% Na_2SO_4) in $NaClO_2$, the scrubbing solution had an initial pH of 10.0.

The actual measurements listed in Table 13 show that NO is quantitatively oxidized to NO_3^- in the liquid during the scrubbing. Hydronium ion was produced to decrease pH to 3 after the first few minutes and 1.8 at the end point of the experiment (Table 14, Figure 7). The end point is reached when NO breaks through.

Table 13 NO Oxidation by $NaClO_2$ in Aqueous Scrubbing

Phase	Item	Expt #1	Expt #2	Expt #3
Gas	Conc. of NO	2,325 ppm	2,075 ppm	2,175 ppm
	Flow rate	1 l/min	1 l/min	1 l/min
	Time (B.K.)	80 min	89 min	88 min
	Moles	0.00759	0.00754	0.00781
liquid	Conc. of $NaClO_2$	0.008 M	0.008 M	0.008 M
	Conc. of Na_2CO_3	0.0015 M	0.0015 M	0.0015 M
	Conc. of Na_2SO_4	0.00038 M	0.00038 M	0.00038 M
	Volume	1 liter	1 liter	1 liter
	pH before	10.1	10.1	10.1
	pH after	1.82	1.99	1.83
	Conc. of NO_3^-	480 ppm	460 ppm	480 ppm
	Mole of Cl^-	0.0080	0.0082	0.0083
	Mole of NO_3^-	0.0077	0.0074	0.0077
	NO/ NO_3^-	0.98	1.02	1.01
	ClO_2^- / Cl^-	1.00	1.03	1.04
	NO/ClO_2^-	0.95	0.94	0.97

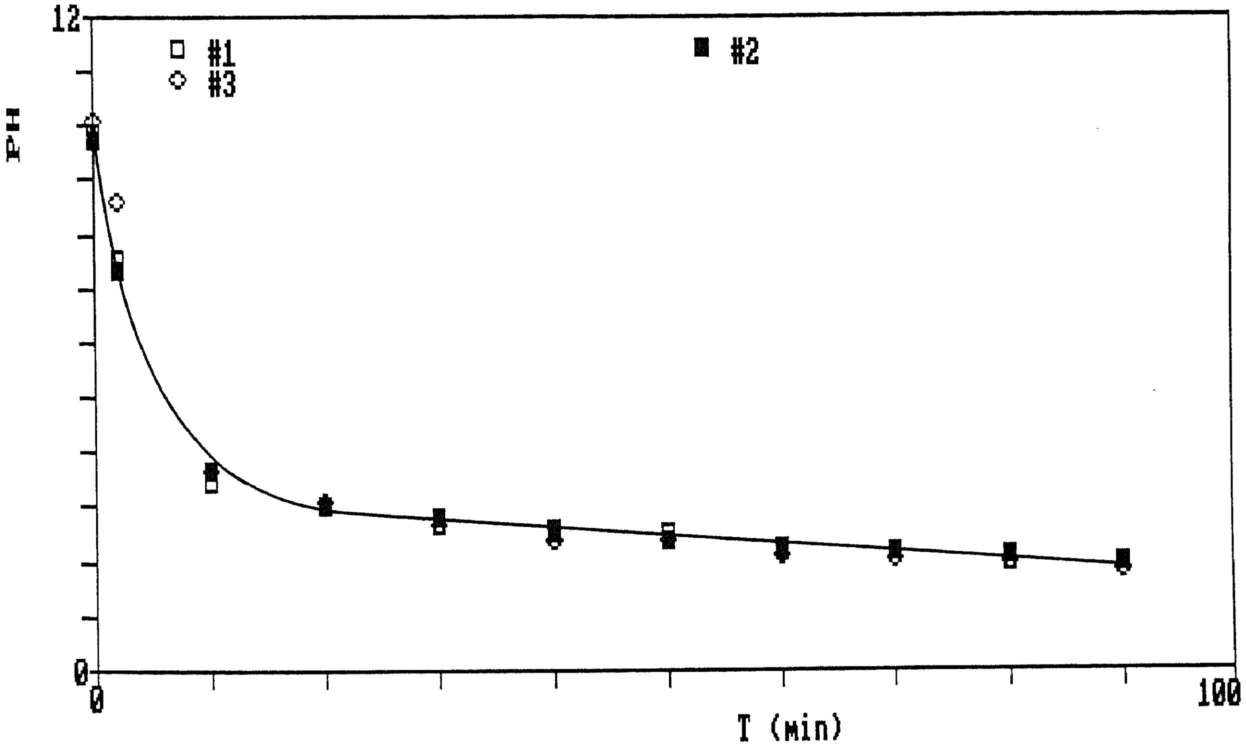
Time (B.K.): Break through time

Effectiveness: $NO/ClO_2^- = 0.95$

Table 14 pH Change in NO Scrubbing with 80% $NaClO_2$ as Received

Sample #	Time (min)	Expt #1	Expt #2	Expt #3
1	0	9.87	9.77	10.10
2	2	7.53	7.31	8.59
3	10	3.49	3.70	3.65
4	20	3.06	3.06	3.01
5	30	2.71	2.80	2.68
6	40	2.57	2.58	2.43
7	50	2.54	2.43	2.38
8	60	2.23	2.20	2.13
9	70	2.16	2.21	2.06
10	80	1.98	2.14	1.96
11	90	1.98	1.98	1.98
12	100	1.93	1.93	1.86

Figure 7 pH Change in NO Aqueous Scrubbing



The second set of experiments were performed to figure out the products formation during the experiment. Experiments were conducted at the following conditions:

Flue gas

NO: 2,000 ppm

Balance: N_2

Flow rate: 1 l/min

Scrubbing solution

$NaClO_2$: 0.008 M

Na_2CO_3: 0.0015 M

Na_2SO_4: 0.00038 M

Volume: 1 liter

Room temperature and atmospheric pressure

Samples were taken out at fixed time interval to determine Cl^- and NO_3^- concentrations by Ion chromatography. Figure 8; derived from Table 15, indicates that the formation rates of both products are constants as the concentration of $NaClO_2$ changes from 0.008 to 0 Molar. This data indicates that mass transfer may be limiting the process.

Table 15 Concentrations of NO_3^- and Cl^- with Respect to Reaction time

Sample #	Time (min)	RT(1) (min)	PA(2) 10^7	Conc. (ppm)	Conc. (M) 10^{-2}
1	0	3.09	3.33	92	0.26
2	3	3.13	3.74	108	0.30
		5.51	0.38	28	0.05
3	20	3.13	5.98	164	0.46
		5.51	2.49	140	0.23
4	40	3.18	8.78	240	0.68
		5.43	5.28	284	0.46
5	52	3.21	10.41	290	0.82
		5.41	7.70	420	0.68
6	61	3.20	10.72	300	0.85
		5.40	7.98	440	0.71
7	70	3.23	10.70	300	0.85
		5.40	8.51	490	0.79
8	75	3.22	10.69	300	0.85
		5.41	8.54	492	0.79

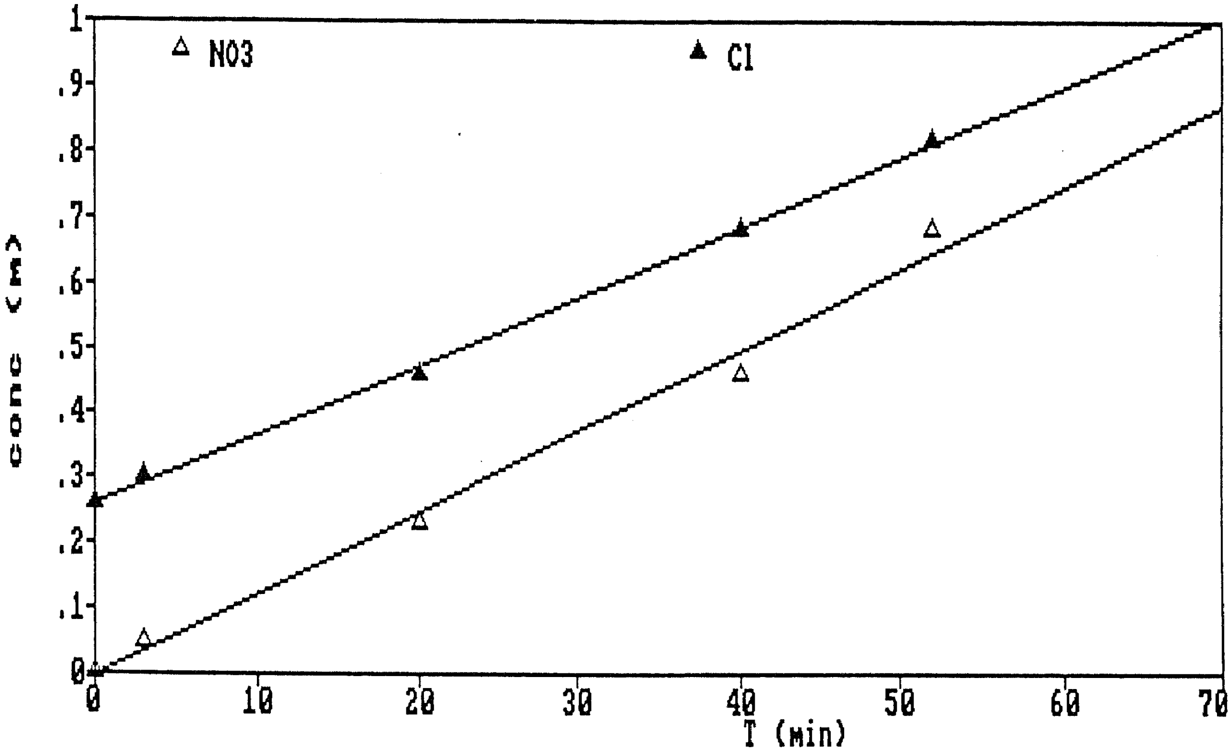
(1) RT: Average retention time

RT of Cl^- is 3.10 to 3.20 minute

RT of CO_3^- is 5.40 to 5.50 minute

(2) PA.: Average Peak area

Figure 8 Concentration-Time Curves of NO Scrubbing



5-6 Oxidation of NO by $NaClO_2$ in Caustic Aqueous Scrubbing

In order to compare the NO absorption effectiveness of caustic scrubbing to neutral solution, several runs were made with NaOH under the following conditions

Flue gas

NO: 2,000 ppm
Balance: N_2
Flow rate: 1 l/min

Scrubbing solution

$NaClO_2$: 0.01 M
Na_2CO_3: 0.0015 M
Na_2SO_4: 0.00038 M
NaOH: 0.001 M
Volume: 1 liter

All experiments were conducted at room temperature and pressure.

Result containing in Table 16 indicate that the effectiveness of NO absorption in $NaClO_2$ aqueous scrubbing was slightly improved (NO/ClO_2^- rise to 1.04) by NaOH addition.

Table 16 Effectiveness of NO Absorption in $NaClO_2$ Caustic Aqueous Scrubbing

Phase	Item	Expt #1	Expt #2	Expt #3
Gas	Conc. of NO	1,950 ppm	1,925 ppm	2,075 ppm
	Flow rate	1 l/min	1 l/min	1 l/min
	Time (B.T.)	104 min	105 min	100 min
	moles of NO	0.0083	0.0083	0.0085
Liquid	Conc of $NaClO_2$	0.0080	0.0080	0.0080
	Conc of Na_2CO_3	0.0015	0.0015	0.0015
	Conc of Na_2SO_4	0.00038	0.00038	0.00038
	conc. of NaOH	0.00097	0.00097	0.00097
	Volume	1 liter	1 liter	1 liter
	pH before	11.27	11.27	11.27
	pH after	1.69	1.75	1.73
	Conc. of NO_3^-	510 ppm	520 ppm	510 ppm
	Mole of Cl^-	0.0083	0.0086	0.0087
	Mole of NO_3^-	0.00823	0.00839	0.00823
	NO/NO_3^-	1.01	0.99	1.03
	Cl^-/ ClO_2^-	1.03	1.05	1.03
	NO/ClO_2^-	1.04	1.04	1.06

5-7 Oxygen Effect on NO Absorption in $NaClO_2$ Aqueous Scrubbing

When flue gas containing O_2 is bubbled through a $NaClO_2$ containing scrubber, $NaClO_2$ may react with O_2. In order to ascertain this effect, several runs were made at the following conditions

Flue gas
    NO: 2,000 ppm
    O_2: 5%
    Balance: N_2
    Flow rate: 1 l/min
Scrubbing solution
    $NaClO_2$: 0.01 M
    Na_2CO_3: 0.0015 M
    Na_2SO_4: 0.00038 M
    Volume: 1 liter

All experiments were conducted at room temperature and pressure.

Table 17 shows that the effectiveness of NO scrubbing by $NaClO_2$ decreased (NO/ClO_2^- drop to 0.84) when O_2 was present in the flue gas.

Table 17 Oxygen Effect on NO Absorption in $NaClO_2$ Scrubbing

Phase	Item	Expt #1	Expt #2	Expt #3
Gas	Conc. of NO	1,883 ppm	1,841 ppm	1,883 ppm
	Flow rate	1 l/min	1 l/min	1 l/min
	Break through	84 min	90 min	90 min
	Mole of NO	0,0065	0.0068	0.0069
Liquid	Conc of $NaClO_2$	0.008	0.008	0.008
	Conc of Na_2CO_3	0.0015	0.0015	0.0015
	Conc of Na_2SO_4	0.00038	0.00038	0.00038
	volume	1 liter	1 liter	1 liter
	mole of ClO_2^-	0.008	0.008	0.008
	NO/ ClO_2^-	0.81	0.85	0.86

5-8 pH Effect on NO Absorption in $NaClO_2$ Aqueous Scrubbing

Based on the results reported in section 5-6, a certain amount of NO breaks through with $NaClO_2$ scrubbing in presence of 0.001M NaOH. It was presumed that NaOH may inhibit or may lower the mass transfer coefficient of this process. In order to ascertain the veracity of this prediction, a number of experiments were performed under the following conditions

Flue gas
  NO: 2,000 ppm
  Balance: N_2
  Flow rate: 1 l/min
Scrubbing solution
  $NaClO_2$: 0.00008, 0.0008, 0.008, 0.08 M
  Na_2CO_3: 0.000015, 0.00015, 0.0015 and 0.015 M
  Na_2SO_4: 0.0000038, 0.000038, 0.00038 and 0.0038 M
  NaOH: 0.0001, 0.001, 0.005, 0.01, 0.1, 1 M
  Volume: 1 liter

All runs were conducted at room temperature and pressure.

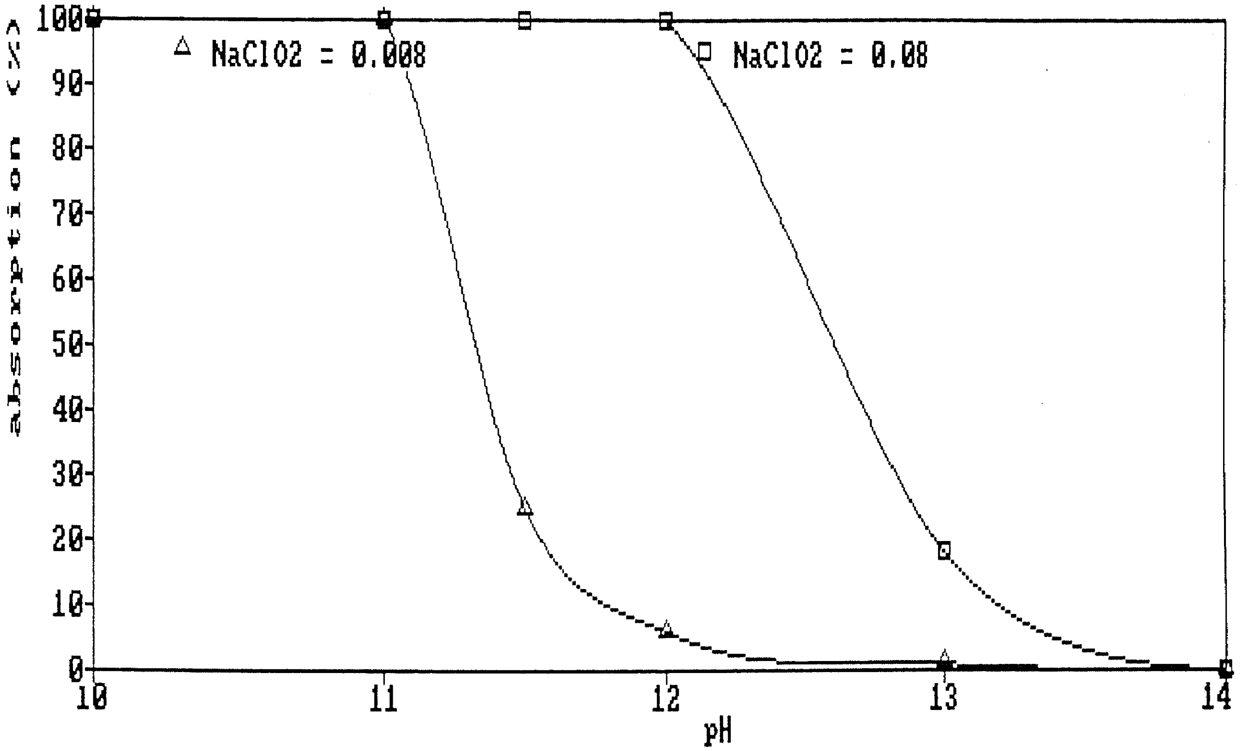
Figure 9, derived from Table 18, indicate that high concentration of NaOH inhibit NO absorption in $NaClO_2$ aqueous scrubbing.

Table 18 pH Effect on NO Absorption in NaClO$_2$ Caustic Aqueous Scrubbing

Conc. of NaOH	Expt #	Per-cent Absorption			
		Conc. of NaClO$_2$			
(M)		0.00008	0.0008	0.008	0.08
0.0001	1	1	0	100	100
	2	2	0	100	100
	3	1	0	100	100
	avg	1	0	100	100
0.001	1	1	0	100	100
	2	0	1	100	100
	3	3	0	100	100
	avg	1	0	100	100
0.005	1	-	-	25	100
	2	-	-	24	100
	3	-	-	25	100
	avg			25	100
0.01	1	0	0	4	100
	2	0	2	6	100
	3	0	1	8	100
	avg	0	1	6	100
0.1	1	1	0	0	17
	2	0	1	0	17
	3	1	1	1	19
	avg	1	1	0	18
1.0	1	0	2	0	0
	2	0	2	1	2
	3	4	1	0	0
	avg	1	2	0	1

$$\text{Absorption } \% = 1 - \frac{\text{NO(out)}}{\text{NO (in)}} * 100\%$$

Figure 9 PH Effect on NO Absorption in $NaClO_2$ Caustic Aqueous Scrubbing



6 DISCUSSION

A semibatch reactor was used to evaluate the potential of oxidizing NO with $NaClO_2$ in an alkaline scrubbing solution. The synthetic flue gas was blended from compressed gas cylinders and was continuously fed to the scrubbing solution which was the stationary phase in the reactor. The flue gas was introduced into the reactor through a polyethylene sparger located at the botton of the reactor. Thus the bubble size was influenced by the pressure of flue gas, the size the sparger openings, and the viscosity of the scrubbing solution.

The absorption of NO by an aqueous solution of alkaline $NaClO_2$ was accomplished at room temperature and 101.3 kPa of flue gas pressure. A greenish yellow color in the solution was found after three minutes of operations and disappeared after 105 minutes. It is assumed that the color represents an intermediate in the absorption of NO. The mole ratio of the total amount of NO that flowed through the reactor to $NaClO_2$ is 0.95 at breakthrough. It should be reemphasized that 80% $NaClO_2$ was used with the rest of the starting material in solution consisting of 18% Na_2CO_3 and 2% Na_2SO_4. Thus, the initial composition of the scrubber liquid was quite alkaline. Under all conditions when $NaClO_2$ was present, the other two reagents were also present. For expediency, this fact may not be mentioned every time $NaClO_2$ chemistry is discussed.

Low concentrations of NaOH increase the NO removal effectiveness. High concentrations of NaOH inhibited the absorption. The upper limit for NaOH concentration necessary to completely absorb NO in $NaClO_2$ aqueous solution depends on the concentration of $NaClO_2$. NO was absorbed quantitatively in 0.008 molar $NaClO_2$ aqueous solution when the concentration of NaOH was equal to or lower than 0.001 molar. The upper limit of NaOH in 0.08 molar $NaClO_2$ aqueous solution is 0.1 molar. At the upper limit concentration of NaOH, absorption can not reach 100% within the first few minutes. If the NaOH concentration is a little higher than upper limit, absorption goes to zero after a few minutes of running time.

NaOH in $NaClO_2$ aqueous solution increases the effectiveness of NO to $NaClO_2$ reactant ratio at breakthrough to 0.96 - 1.05 while 5% oxygen in the flue gas decreases it to 0.84.

Before saturation, the concentration-time curves are straight lines of different slopes. Slope of NO_3^- is greater than that of Cl^-. The rate of formation of NO_3^- is faster than that of Cl^-. The time between their formation is the life time of the green intermediate.

The pH value of the aqueous solution drops drastically from 10 to 3 within the first ten minutes. The solution was prepared with 0.008 molar of $NaClO_2$ and 0.0015 molar of Na_2CO_3 owing to the 18% (w/w) and 2% Na_2SO_4 impurity. The pH value of this solution is 10. After three minutes running, the reaction was carried out under acidic condition.

After $NaClO_2$ in scrubbing solution was used up, only two products were found in the scrubbing solution. They were NO_3^- and Cl^-. The CO_3^{-2} converted to H_2CO_3 when pH fell below 3. The pH value of the scrubbing solution is 1.9. Under this situation, no CO_3^{-2} exisit in the solution. Since no CO_3^{-2} signal is found in ion chromatography.

7 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORKS

7-1 Conclusions

A series of experiments were performed in order to evaluate the capability of alkaline $NaClO_2$ aqueous solution to scrubb NO by oxidizing it from synthetic flue gas. In some runs, NO_2 or O_2 were mixed into the synthetic flue gas to simulate the flue gas emitted by municipal incinerator or stationary power plant. The conclusions from this research are listed as below:

* At room temperature and atmospheric pressure, NO is not absorbed by distilled water. NaOH up to 1.0 molar does not improve this absorption.
* At room temperature and atmospheric pressure, NO_2 can be absorbed effectively by NaOH aqueous solution. A 0.5 molar NaOH aqueous solution can scrubb 98% of NO_2 from flue gas at relatively low NO_2 concentration (lower than 800 ppm).
* The effectiveness of NO absorption in caustic aqueous scrubbing is greatly increased by the presence of NO_2 in the flue gas.
* 5% O_2 in flue gas does not affect NO absorption in caustic (NaOH up to 1.0 molar) aqueous scrubbing.
* NO can be oxidized effectively by $NaClO_2$ in aqueous solution. During scrubbing, NO is oxidized to NO_3^-, and ClO_2^- converted to Cl^- in scrubbing solution.

- Owing to the production of HNO_3, pH drops sharply from 10 to 3 within ten minutes in the scrubbing of NO by alkaline $NaClO_2$ aqueous solution.
- Rates of Cl^- and NO_3^- formation in scrubbing solution are constants at the low concentration scrubbing process as the concentration of $NaClO_2$ changes from 0.008 molar to 0 molar.
- Low concentration of NaOH increase the effectiveness of NO absorption in $NaClO_2$ aqueous scrubbing solution by 7%, while concentrations higher than upper limit decreases or inhibits its absorption.
- Effectiveness (NO/ClO_2^- ratio) decrease from 0.95 to 0.84 when 5% O_2 in presence of flue gas.

7-2 Recommendations for future works

The results of this program clearly indicates the utility of $NaClO_2$ for NO_x emission control. The best conditions of chemical reaction of NO_x in $NaClO_2$ and aqueous scrubbing can be reached from the results presented in this thesis. However, to develop the engineering data that is essential for scale-up, pilot plant studies are needed . Some critical factors which need to be studied in pilot plant process are listed below:

- Rate of NO absorption in alkaline $NaClO_2$ aqueous solution in pilot plant conditions.
- The overall mass transfer coefficient and interfacial area

of pilot plant process.

* How does temperature affect this process in pilot plant conditions

* How do other flue gas components affect the NO absorption in $NaClO_2$ aqueous scrubbing.

* Optimization should be assessed.

* How to treat the scrubbing solution (pH of 1.8 and NO_3^-).

The purposes of this progrem should be to completely remove NO_x from flue gas and the effect of scrubbing solution must be minimized to meet the regulations at the same time.

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